

# STRUCTURE EVOLUTION DURING FERROELECTRIC PHASE TRANSITION IN A VINYLIDENE FLUORIDE/TRIFLUOROETHYLENE COPOLYMER

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## Introduction

There have been intense scientific and technological interests in vinylidene fluoride and trifluoroethylene (PVDF/TrFE) copolymers during the past two decades.<sup>1-3</sup> This is because these materials exhibit a unique transition between ferroelectric and paraelectric phases. They also have strong piezoelectricity and pyroelectricity, suitable for numerous electrical applications. The above transition appears to be dependent on the VDF content, crystallization temperature and annealing treatment conditions. While the molecular structures and dynamics of the two phases have been established,<sup>4-6</sup> the transition kinetics remains unclear. In this study, the kinetics of ferroelectric to paraelectric transition in a copolymer of PVDF/TrFE with composition (VDF/TrFE = 65/35 by mole) was studied by differential scanning calorimetry (DSC) and the structural evolution was followed by time-resolved synchrotron simultaneous small-angle X-ray scattering and wide-angle X-ray diffraction (SAXS/WAXD) techniques.

## Experimental\*

The PDVF/TrFE copolymer used in this study had 65 mole % VDF, which was kindly supplied by Mr. Thomas Ramotowski of the Naval Undersea Warfare Center (NUWC), Newport, RI.\* The melting temperature ( $T_m$ ) of this copolymer was approximately 158 °C by DSC (at 2 °C/min). The sample was first melt-pressed into a disc shape with diameter of 7 mm and thickness of 1.5 mm, and then kept at 185 °C for 10 min and followed by quench into a thermal bath maintained at the isothermal crystallization temperature. The following isothermal crystallization temperatures were used 74 °C, 91 °C, 106 °C, 120 °C, 140 °C and 151 °C. The uncertainty of temperature is 1 °C. The crystallization time was 24 h. A DSC 2820 Module controlled with Thermal Analysis 2200 (TA Instruments) was used for DSC measurement.\* The sample quantity was 6 mg to 8 mg. The heating rate was kept at a 2 °C/min.

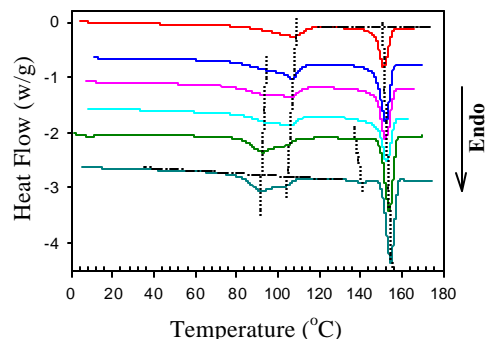
Time-resolved simultaneous small-angle X-ray scattering and wide-angle X-ray diffraction measurement was performed at the Advanced Polymers Beamline (X27C) in National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL).\* The detailed experimental setup for SAXS/WAXD and the high temperature cell have been described in previous publications.<sup>7-8</sup> The sample was heated from 40 °C to 170 °C at a rate of 2 °C/min. The time-resolved simultaneous SAXS/WAXD measurements were performed with a data acquisition time of 30 s per scan. The sample-to-detector distances for SAXS was 1925 mm and for WAXD was 200 mm.

## Results and Discussion

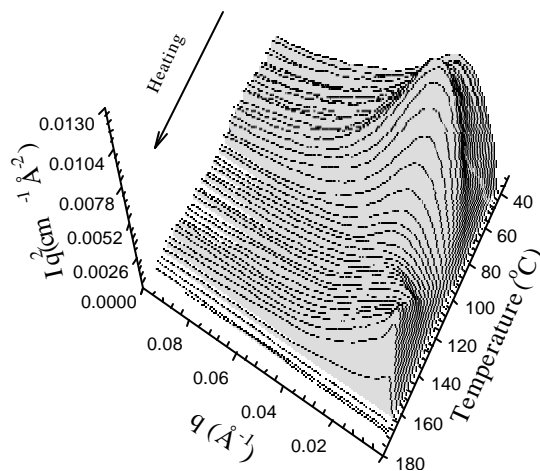
**Figure 1** shows a series of DSC thermograms from samples crystallized at different isothermal crystallization temperatures. The endothermic peaks at the lower temperatures ranged from 75 °C to 120 °C correspond to the ferroelectric-paraelectric phase transition, or the Curie transition. The peaks at higher temperatures ranged from 145 °C to 160 °C correspond to the melting points ( $T_m$ ) of the crystalline phase for samples of different crystallization temperatures. There are two endothermic peaks in the Curie transition region except for the samples crystallized at 74 °C and 91 °C. This observation has been attributed to two different ordered structures formed in the sample if the crystallization temperature is higher than the Curie transition temperature.<sup>6</sup> These peak positions shift to lower temperatures with the increase of isothermal crystallization temperature. In contrast, the melting points are

found to shift to higher temperatures as usually observed in typical semi-crystalline polymers.

**Figures 2 and 3** illustrate typical Lorentz-corrected SAXS ( $Iq^2$  versus  $q$ , the scattering vector) and WAXD profiles during temperature scanning from 40 °C to 170 °C for the sample crystallized at 140 °C. The enhanced WAXD profiles during the Curie transition region are shown in **Figure 4**. From SAXS and WAXD profiles, the integrated scattering intensity, long period estimated by the Bragg law ( $L_B$ ) from SAXS and the d-spacings from WAXD peak positions ( $2\theta$ ) estimated also by the Bragg law have been obtained, which are shown in **Figures 5 and 6**, respectively. The data analysis procedures for calculating these variables can be found in our previous publication.<sup>7-8</sup>



**Figure 1.** DSC heating scans from PVDF/TrFE copolymer crystallized at various temperatures (74 °C, 91 °C, 106 °C, 120 °C, 140 °C and 151 °C, from top to bottom). The curves are shifted in the vertical direction for display.

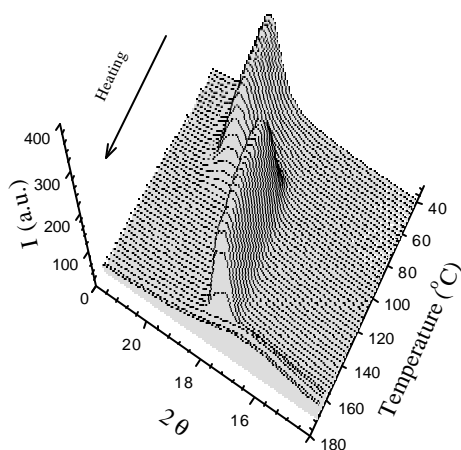


**Figure 2.** Lorentz-corrected SAXS profiles during heating process for the sample crystallized at 140 °C for 24 h (the heating rate was 2 °C/min).

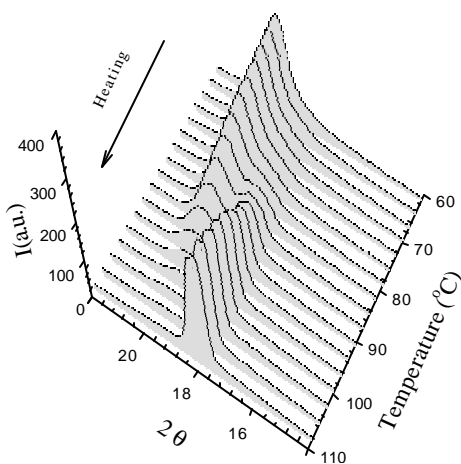
It is seen that marked changes in both structure and lamellar morphology occur in the Curie transition region. For example, during transition, a significant drop of the SAXS integrated intensity after the initial increase is found in all samples (**Figure 5**). The evolution of the lamellar long period shows a transition in samples crystallized at 123 °C and 140 °C, respectively, and a less noticeable transition for the sample crystallized at 74 °C. The long period continues to increase after the Curie transition, and it becomes too large to be measured by the current SAXS setup before final melting. **Figure 4** (the WAXD profile) shows that the intensity of the higher angle diffraction peak gradually decreases with increasing temperature. A lower angle diffraction peak occurs abruptly around 78 °C and its intensity increases with

\* The references to commercial equipment or materials do not imply recommendation or endorsement by the National Institute of Standards and Technology.

temperature. The evolution of the d-spacings corresponding to these two peaks (in Å) is displayed in **Figure 6** (onset temperatures of this transition are marked by dash lines). From DSC, SAXS and WAXD results, it is found that in the Curie transition region, the density fluctuations and structural parameters including long periods by SAXS and characteristic d-spacings by WAXD all change significantly. These changes indicate that there is a coexistence of ferroelectric and paraelectric phases throughout the Curie transition.



**Figure 3.** WAXD profiles during the heating for the sample crystallized at 140 °C for 24 h (the heating rate was 2 °C/min).

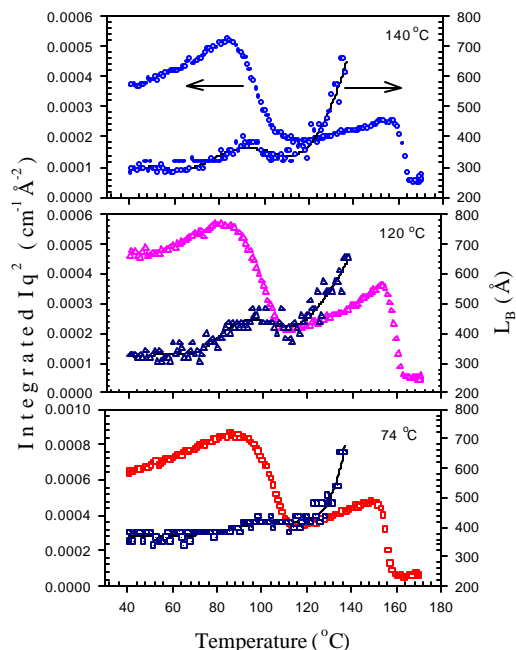


**Figure 4.** WAXD profiles during the Curie transition region for the sample crystallized at 140 °C for 24 h (the heating rate was 2 °C/min).

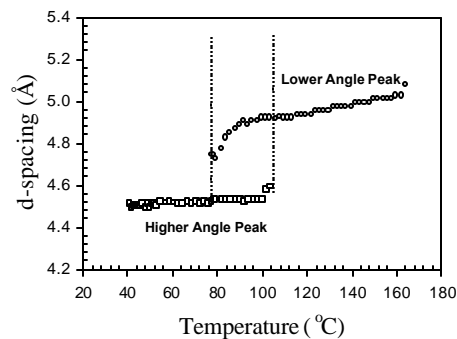
## Conclusions

Results from DSC, SAXS and WAXD provide some new insights into the evolution of structural variables during Curie transition in PVDF/TrFE copolymer. The differences of long period evolution between the melt-crystallized samples in the paraelectric phase (> 80 °C) and in the ferroelectric phase (74 °C) are observed for the first time in the Curie transition region for this copolymer. The decrease in the SAXS intensity indicates that the electron density of the paraelectric phase is less than that of the ferroelectric phase.

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**Figure 5.** Evolution of integrated  $Iq^2$  and  $L_B$  during heating for the samples crystallized at 74 °C, 120 °C and 140 °C, respectively (the relative standard uncertainties of integrated  $Iq^2$  and  $L_B$  are less than 2 % and 1 %, respectively, and are estimated by the relative standard deviations. The solid lines through the data are obtained by polynomial fitting).



**Figure 6.** The changes of d-spacings from the WAXD reflection peaks during heating for the sample crystallized at 140 °C (the relative standard uncertainty of  $2\theta$  is less than 1 %).

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